Photolysis of Benzaldehyde in Solution: the Products

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Summary Benzaldehyde when irradiated in benzene yielded almost equal amounts of benzoin (I), deoxybenzoin (II), and 1,2-diphenylethane-1,2-diol (III); in ethanol the main product was (III) with only a trace of (I); while in hex-1-yne, seven isolable products were (I), (II), (III), heptanophenone (IV), *cis*-hept-2-enophenone (V), *trans*-hept-2-enophenone (VI), and 2-n-butyl-1,4-diphenylbutane-1,4-dione (VII).

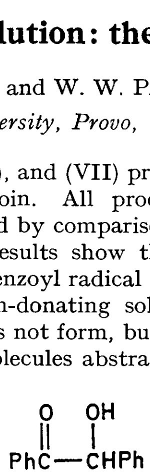
Benzaldehyde has recently been irradiated in solution in order to study the chemically induced dynamic nuclear spin polarization (CIDNP).[1] It was shown that excited triplet benzaldehyde abstracted a hydrogen atom from a ground state benzaldehyde molecule and a radical pair was formed. The radical pair collapsed to form benzoin.[1] The reaction was reversible as shown by the fact that benzoin, on irradiation, formed the same radical pair.[1] No products were isolated.

Benzaldehyde has also been shown to be a product in the photochemical induced cleavage of alkyl aryl ketones.[2] We feel that a knowledge of the benzaldehyde photoproducts is necessary for an understanding of reactions which lead to the formation of benzaldehyde or benzoyl radicals.

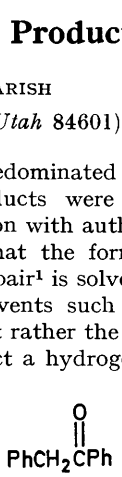
We have irradiated a dilute solution of benzaldehyde in benzene and ethanol as well as a 1—2 molar mixture of hex-1-yne and benzaldehyde. Benzoin (I) was the initial major product of the reaction in benzene only. Also in benzene, a 14 h irradiation yielded almost equal amounts of (I), (II), and (III). At longer irradiation times the benzoin slowly disappears. The irradiation of benzoin in benzene gave first benzaldehyde and then (II) and (III) at longer irradiations. The irradiation of benzaldehyde in ethanol yielded (III) with only a trace of (I).

The photoreaction of the benzaldehyde–hex-1-yne mixture was the most interesting. In addition to (I) (6%), (II) (2%), and (III) (2%), (IV) (3%), (V) (27%), (VI) (24%), and (VII) (29%), were also isolated after 7·5 h irradiation. Other products were formed in such small yields that they could not be isolated. At short irradiation times, products (V), (VI), and (VII) predominated with only small amounts of benzoin. All products were isolated by g.l.c. and identified by comparison with authentic samples.

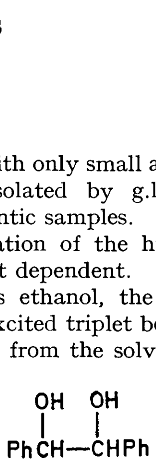
Our results show that the formation of the hydroxybenzylbenzoyl radical pair[1] is solvent dependent. In good hydrogen-donating solvents such as ethanol, the radical pair does not form, but rather the excited triplet benzaldehyde molecules abstract a hydrogen from the solvent and form diol (III).[3] In hex-1-yne, addition to the alkyne competes with both radical pair formation and hydrogen abstraction.


$\mathrm{Ph\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{C}HPh}$

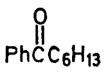
(I)


$\mathrm{PhCH_2\overset{\overset{O}{\|}}{C}Ph}$

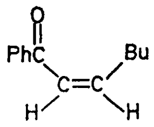
(II)


$\mathrm{Ph\overset{\overset{OH}{|}}{C}H-\overset{\overset{OH}{|}}{C}HPh}$

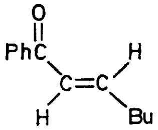
(III)


$\mathrm{Ph\overset{\overset{O}{\|}}{C}C_6H_{13}}$

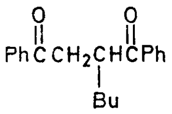
(IV)



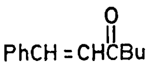
(V)



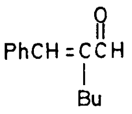
(VI)


$\mathrm{Ph\overset{\overset{O}{\|}}{C}CH_2\underset{\underset{Bu}{|}}{C}H\overset{\overset{O}{\|}}{C}Ph}$

(VII)


$\mathrm{PhCH{=}CH\overset{\overset{O}{\|}}{C}Bu}$

(VIII)


$\mathrm{PhCH{=}\underset{\underset{Bu}{|}}{C}\overset{\overset{O}{\|}}{C}H}$

(IX)

Cycloaddition of benzaldehyde with alkenes to form oxetan products has been shown to be a triplet state reaction.[4] Buchi and his co-workers have observed a similar addition to acetylenic compounds. The resulting oxeten intermediate either rearranged to an unsaturated ketone or decomposed to starting materials.[5] The expected unsaturated ketone in our reaction (resulting from an oxeten intermediate) would not be (V) or (VI) but either (VIII) or (IX). Compounds (VIII) and (IX) were not found in our reaction mixture. Thus, the heptano- and hepteno-phenones as well as diketone (VII) are formed by a different process.

Compounds (V) and (VI) are probably formed by the addition of the benzoyl radical[6] (Type I cleavage product of benzaldehyde) to hex-1-yne. The heptanophenone (IV) product is a simple reduction of the heptenophenones (V and VI).[7] The dione (VII) results from the addition of the benzozyl radical to (V) and (VI). Irradiation of a mixture of (V) and (VI) and benzaldehyde resulted in the formation of (VII).

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[7] This type of process has been observed previously; see G. W. Griffin and E. J. O'Connell, *J. Amer. Chem. Soc.*, 1962, **84**, 4148.